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**RUTHENIUM OXIDE ELECTROCHEMICAL SUPER CAPACITOR OPTIMIZATION
FOR PULSE POWER APPLICATIONS**

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EXECUTIVE SUMMARY

Power sources for electrical actuation systems need to be made as compact as possible for many potential applications. Size and weight constraints require that the energy and power densities of the source be as large as possible. While, in general, it is not possible to optimize both these parameters simultaneously, the electrode fabrication processes for electrochemical capacitors developed here at Auburn University's Space Power Institute offers an excellent combination of the desirable energy and power density characteristics required in a source for these applications. The research effort described here focused on developing the procedures for using hydrous ruthenium oxide (HRO) in electrochemical capacitors. The energy storage mechanism for this material is a redox reaction and is similar to the reaction that occurs in batteries; however, the discharge mechanism follows a profile similar to a capacitor discharge. Thus, these devices are typically referred to as "pseudocapacitors." In this research effort, thick film coating technologies were studied for developing capacitor electrodes that reduce the need for pressure to lower the internal resistance of the device. The effects of electrolyte type, separator membrane material, coating thickness, and geometry were studied. The performance of single-cell capacitor devices was characterized for various combinations of electrolytes, separators, thicknesses, and geometries of the electrodes. As a result of this research effort, new electrolytes that will work with the hydrous ruthenium oxide material were identified. Though these electrolytes did not perform as well as the sulfuric acid (H_2SO_4) typically used in ruthenium oxide devices, they could simplify the packaging requirements of devices since they are less corrosive than the sulfuric acid and are worth further investigation for use in these devices. Also, separators were found that lower the internal resistance and leakage currents for the single-cell tests that were performed here. Using the new separator material, the effects of coating thickness and geometry on the capacitor performance were characterized.

INTRODUCTION

Electrical actuator systems are being pursued as alternatives to hydraulic systems to reduce maintenance time, weight and costs while increasing reliability. Additionally, safety and environmental hazards associated with the hydraulic fluids can be eliminated. For most actuation systems, the actuation process is typically pulsed with high peak power requirements but with relatively modest average power levels. The power-time requirements for electrical actuators are characteristic of pulsed power technologies where the source can be sized for the average power levels while providing the capability to achieve the peak requirements.

Among the options for the power source are battery systems, capacitor systems or battery-capacitor hybrid systems. Battery technologies are energy dense but deficient in power density; capacitor technologies are power dense but limited by energy density. The battery-capacitor hybrid system uses the battery to supply the average power and the capacitor to meet the peak demands. It has been demonstrated in previous work that the hybrid electrical power source can potentially provide a weight savings of approximately 59% over a battery-only source.^{1,2}

Electrochemical capacitors have many properties that make them well-suited for electrical actuator applications. They have the highest demonstrated energy density for capacitive storage (up to 100 J/g), have power densities much greater than most battery technologies (>30kW/kg), are capable of greater than one million charge-discharge cycles, can be charged at extremely high rates, and have non-explosive failure modes.³⁻⁶ Thus, electrochemical capacitors exhibit a combination of desirable battery and capacitor characteristics.

BACKGROUND

In the 1970's, B. E Conway, at the University of Ottawa, discovered that an extremely fast redox reaction was possible at the surface of some low resistivity oxides. This discovery led to the development of an electrochemical capacitor based on the intercalation of hydrogen ions (protons) into a surface to produce charge separation. For this technique to be successful, there must be a ready source of hydrogen ions in the electrolyte solution. For best performance, acid or hydroxide electrolyte solutions are used, the most common being sulfuric acid and potassium hydroxide. While many of the oxides will perform satisfactorily, the most common oxide is ruthenium which exhibits the highest energy storage density for capacitors and is capable of delivering that energy at a rate up to 30 kW/kg. More recently, the Army Research Laboratory developed a hydrous version of the ruthenium technology that doubled the energy density associated with crystalline ruthenium oxide-based electrochemical capacitors. The energy density is factors of 3-4 greater than carbon technology. Auburn University's Space Power Institute has developed coating processes for making electrochemical capacitors using this material. Ruthenium oxide capacitors have been constructed that exhibit energy storage densities three to four times greater than that of carbon-based electrochemical capacitors. These RuO_2 capacitor devices have been physically small because the processing techniques used to construct them require pressure to minimize internal resistance. Crimp-can packaging, which is used to place uniform pressure across the capacitor "cell," is typically no larger than about 1.5 inches in diameter. Devices with a larger cross-sectional area require heavy pressure plates and torque bolts to apply the needed uniform pressure. This heavy hardware, however, erodes the gains made in energy density.

The launch vehicle designs and existing vehicle upgrade efforts that are ongoing have plans for use of electromechanical actuation to replace hydraulics for aerosurface and thrust vector control applications. In so doing, the high operational costs associated with hydraulics can be eliminated. There is, however, a challenge posed by electrical actuation and that is the requirement of high pulse power demands of these devices. Conventional power sources are no longer sized by the amount of energy required, but by the peak power demands. This results in a power source that is heavier than desired. Tests performed at NASA's Marshall Space Flight Center have verified the concept of using supercapacitors in parallel with a conventional power source, such as an electrochemical battery, to produce a hybrid source that possesses both the high power density performance of the supercapacitors, and the high energy density performance of a battery. This testing showed that hybrid power sources can be sized that are almost 60% lighter than a battery sized for the same application.¹

Hydrous ruthenium oxide pseudocapacitors have been built which exhibit an energy storage density of approximately 100J/g for the active material (ruthenium oxide). This value is approximately twice the value that has been obtained using crystalline ruthenium oxide.

Amorphous hydrous-ruthenium oxide supercapacitors have demonstrated high energy and power densities. The thin-coated amorphous $\text{RuO}_2 \cdot x\text{H}_2\text{O}$ electrode that was developed by Space Power Institute at Auburn University makes the hydrous ruthenium oxide supercapacitor even more attractive for many applications. As part of this research effort, the performance of the supercapacitor (such as ESR, capacitance, frequency response, and impedance spectra etc.) using various types of electrolytes, separators,

coating thicknesses, and geometry were investigated.

In recent years ruthenium oxide and its hydrate have been found to be excellent materials for high energy density electrodes because of their high capacitance and low resistance.^{7,8} The outstanding capacitance properties of ruthenium oxide are postulated to arise in part from multiple oxidation states of ruthenium and the facile conversion of ruthenium from one oxidation state to another, and in part to proton mobility between the oxide and hydroxyl sites in hydrated ruthenium oxide. However, the observed capacitance of ruthenium oxide is quite dependent on its physical state. In particular, it has been recognized that high capacitance requires that ruthenium oxide be in the amorphous state with an appropriate degree of hydration. In addition, capacitance of the hydrated ruthenium oxide has shown an excellent high frequency response.

Hydrous ruthenium oxide has high energy and power density and fast frequency response. The key issue is how to use this material to fabricate a high performance capacitor. A typical method for fabricating supercapacitors employs die-press technology in which a powder material is layered with spacers, current collectors, ion-permeable separator, and electrolyte, and the assembly is then pressed to high pressure and sealed in a case. The seal is usually crimped or welded to keep the contents under pressure. Pressure is required during fabrication and storage in order to assure good interparticle contact so as to minimize the internal resistance. There are two major problems related to this process: one is the constant pressure needed in order to keep the electrode at a low resistance, and the second is the difficulty to produce consistent and uniform cells. In addition, the die press method is not amenable to mass production-manufacturing techniques. Besides the processing method, other factors, such as the method used for fabrication of electrode, the types of separator, types of electrolytes, end plates, etc., can have significant impact on the performance of a final product. In this research effort, a coating technology was employed to fabricate hydrous ruthenium electrodes. The effects of electrode composition and types of separators on the supercapacitor are discussed.

STATEMENT OF WORK

Ruthenium Oxide (RuO_2) capacitors have been constructed that exhibit energy storage densities three to four times greater than that of carbon-based electrochemical capacitors. Techniques have been employed to fabricate RuO_2 capacitors that require minimal pressure to lower the equivalent series resistance (ESR) and improve energy density performance. Further effort needs to be done to optimize design parameters of these electrochemical capacitors such as electrolyte type, separator material, electrode active material thickness, and electrode geometry to arrive at the best power and energy density numbers.

In this research effort, techniques, processes, and materials were investigated to optimize hydrous ruthenium oxide electrochemical capacitors' capacitance, ESR, leakage current, and power and energy density parameters. For uniformity purposes, electrode shape was constant while evaluating the effects of different electrolytes, separators, and coating thickness on the performance of the capacitors constructed. For these tests, the electrode size used was a 1.25" x 1.25" square (3.2 cm x 3.2 cm). The following tasks were performed to analyze the effects of electrolytes, separator material, electrode coating thickness, and electrode geometry on the capacitor performance.

Task 1: Influence of Separators on Capacitor Performance

The battery industry has been investing huge R&D money from government and private sectors to continue developing and improvement of battery performance such as reducing the internal resistance to increase pulse performance. In order to compete with new batteries, the capacitor pulse power performance needs to be improved. One of major factors determines the pulse performance is the separator conductivity and stability. We are going to investigate three different separators that have different porosity (from 15% to 50%) and different thickness (from 12 μm to 25 μm) to see how these factors affect the pulse performance and the internal resistance of the devices. In addition, the cost is another important factor will be addressed in determination of separator for HRO capacitor. The separators used in this analysis were a fiberglass-based separator, a polyethylene-based separator, a polycarbonate-based separator, and a proprietary separator from a supplier who prefers not to be disclosed at this time. The results for the different types of separators are shown in Table 1. The equivalent series resistance (ESR) was measured at 1 kHz (typical measurement point used by industry) and at 0.01 Hz (essentially dc value better suited for the proposed actuation applications). Also, the capacitance and leakage current measured after applying the rated voltage for 30 minutes are shown in the table. The proprietary separator material showed the best overall performance by having the lowest internal resistance and lowest leakage current of all the separator materials used. This separator was then used to study the effects of electrolytes, electrode thickness, and geometry on capacitor performance.

Table 1. Evaluation of Separators on Capacitor Performance

Type of Separator	ESR (m Ω)@1Khz	ESR (Ω)@0.01hz	I _{Leakage} (mA) @ 30min. @ V	Capacitance (F)	Comments
Fiberglass					
Average	84.67	0.32	3.77	5.77	
Standard Deviation	12.01	0.18	1.23	0.25	
Celgard					
Average	100	0.62	7.00	5.93	
Standard Deviation	8.54	0.35	5.58	0.12	
Polycarbonate					
Average	69	0.31	2.58	5.6	
Standard Deviation	3.61	0.08	0.77	0.17	
Proprietary Separator					Proprietary separator shows the best consistence and overall performance
Average	63.67	0.30	0.54	5.5	
Standard Deviation	3.21	0.09	0.13	0.4	

Task 2: Effects of Electrolytes

The hydrous ruthenium oxide capacitors were tested using several different electrolytes. Typically, sulfuric acid (H_2SO_4) is always used as the electrolyte because it has the highest conductivity, and good low temperature performance. The primary disadvantage of using H_2SO_4 electrolyte is that few of materials are compatible with H_2SO_4 because it is extremely corrosive. This results in a limited material selection for capacitor manufacture. This study is looking for alternative electrolytes which are less corrosive and more compatible with other materials such adhesive sealing, current collector, packaging, and separator. Because of the nature of HRO redox process, the proton is required. In this effort, we investigated both aqueous and non-aqueous (~5% water moisture) electrolytes. In addition to the sulfuric acid typically used, we looked at potassium hydroxide (KOH), phosphoric acid (H_3PO_4), triflic acid, lithium ion, and an organic electrolyte. With this experiment, we should be able to get some idea of the feasibility of alternative electrolyte for HRO capacitors. Using less corrosive electrolytes could help to simplify the manufacturing procedures used to produce these capacitors. Table 2 summarizes the data taken for the tests using the various electrolytes. The triflic acid was not compatible with the electrode materials. It was corrosive and attacked the electrode materials; thus, a cell could not be constructed and no data was obtained using this electrolyte. The electrode materials were not stable in potassium hydroxide (KOH), either. Though data was obtained using the KOH, for stability reasons, it is not a viable choice of electrolyte for the HRO capacitors. Likewise, the organic electrolyte was not compatible with the polymer current collector typically used, but it did work with

titanium foil as the current collector. However, the ESR of the device was significantly higher than the other suitable electrolytes. The lithium ion electrolyte was shown to work with the electrode materials, though its performance was not as good as other electrolytes. Increasing the concentration of Li ions could possibly improve its performance and may be worth investigating in future research efforts. Though the sulfuric acid still had the best performance of all the electrolytes tested, other electrolytes which will work with the HRO devices were identified. The performance of phosphoric acid was comparable to the sulfuric acid and is much less corrosive. Its use could ease the manufacturing and packaging requirements of devices and is worthy of further investigation for use in these devices.

Table 2. Performance of HRO Capacitors Using Various Electrolytes

Type of electrolyte	ESR (mΩ)@1Khz	ESR (Ω)@0.01hz	I _{Leakage} (mA) @ 30min. @ V	Capacitance (F)	Comments
6M H₃PO₄					
Average	102	0.30	0.40	5.23	Works well with electrode materials
Standard Deviation	34.12	0.05	0.052	0.23	
2M Li-ion					May need increase the concentration of Li-ions
Average	112.33	4.33	1.09	1.57	
Standard Deviation	28.43	0.58	1.22	0.06	
Triflic acid					Too corrosive to handling and attacking the electrode materials
Average					
Standard Deviation					
Organic					Not compatible with polymer current collector materials, but works well with Ti foil.
Average	830.33	9.65	0.32	1.29	
Standard Deviation	74.22	0.67	0.045	0.079	
27wt% KOH					Electrode materials not stable in KOH
Average	142.33	0.59	53.88	4.80	
Standard Deviation	69.51	0.27	44.41	~0	
6M H₂SO₄					Works well with electrode materials
Average	63.67	0.30	0.54	5.5	
Standard Deviation	3.21	0.09	0.13	0.4	

Three samples were tested in each group, and 3.2cmx3.2cm electrode size was used.

Task 3: Electrode Active Material Thickness Comparison

Using the proprietary separator and 6M H₂SO₄, the effect of electrode thickness on capacitor performance was characterized. The coating thickness was controlled by the screen mesh size used in the coating process and by making multiple passes during the coating process. During these tests, the coating thickness was varied from 0.5 mils (0.0005 inches) to 4.7 mils. Part of the objective of this task was to develop the capability to control the coating thickness so that capacitor parameters could be tailored for a particular application. The results are shown in Table 3. Increasing the electrode thickness increased the capacitance of the device. However, the leakage current increased as well and this would have to be accounted for in a system design.

Table 3. Effect of the Electrode Thickness on Capacitor Performance

Thickness (mils)	ESR (mΩ)@1Khz	ESR (Ω)@0.01hz	I _{Leakage} (mA) @ 30min. @ V	Capacitance (F)	Comments
4.7					Leakage current increases as the increase of the thickness
Average	67.66	0.21	7.00	19.73	
Standard Deviation	1.53	0.01	0.43	0.64	
95% Confidence	67.66±1.73	0.21±0.01	7.00±0.48	19.73±0.73	
2.9					
Average	68.00	0.33	1.13	13.03	
Standard Deviation	1.00	0.06	0.06	0.93	
95% Confidence	68.00±1.13	0.33±0.01	1.13±0.07	13.03±1.05	
0.9					
Average	66.67	0.30	0.47	5.5	
Standard Deviation	2.08	0.09	0.02	0.40	
95% Confidence	66.67±2.36	0.30±0.10	0.47±0.02	5.5±0.45	
0.5					
Average	61.66	0.60	0.22	1.30	
Standard Deviation	2.08	0.13	0.04	0.09	
95% Confidence	61.66±2.36	0.60±0.15	0.22±0.04	1.30±0.10	

Three samples were tested in each group, and 3.2cmx3.2cm electrode size was used for making cells, and proprietary separator and 6M H₂SO₄ were used in these cells.

Task 4: Electrode Geometry Comparison

To test the effects of electrode shape and geometry on capacitor performance, electrodes were constructed with a constant area in circular, square, and rectangular shapes. The results are shown in Table 4. The capacitance was consistent for each of the electrode shapes, though there was some variation in the ESR. This variation is likely due to the pressure distribution across the electrode area. Even through our innovative technology is able to reduce the pressure needs for the capacitors in terms of low

achievable ESR, the non-uniform pressure distribution may affect the stability and repeatability of the capacitor performance, especially in high power application. The differences can likely be attributed to the assembly/packaging techniques used for the different geometries.

Table 4. Effect of Electrode Shape n Capacitor Performance

Shape of electrode	ESR (m Ω)@1Khz	ESR (Ω)@0.01hz	I _{Leakage} (mA) @ 30min. @ V	Capacitance (F)
Circle				
Average	176.00	0.74	0.19	1.31
Standard Deviation	42.04	0.18	0.06	0.07
Rectangle				
Average	97.00	0.53	0.22	1.32
Standard Deviation	21.63	0.06	0.081	0.10
Square				
Average	158.33	0.52	0.33	1.36
Standard Deviation	29.78	0.08	0.12	0.06

*Three samples were tested in each group, and proprietary separator and 6M H₂SO₄ were used in these cells.

SUMMARY/CONCLUSIONS

The hydrous ruthenium oxide electrochemical capacitor performance has been characterized for a variety of electrolytes, separator materials, coating thickness, and geometry. As a result of this study, new separator materials that improve the performance of the devices were identified. Also, alternative electrolytes that are less corrosive than sulfuric acid were found to have acceptable performance when used in these capacitors. They could simplify the assembly and packaging procedures associated with these capacitors. However, the sulfuric acid was still found to have the best overall performance for these devices and materials that are compatible with it should still be developed and used if possible.

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